Electrochemical Water Splitting Coupled with Organic Compound Oxidation:

The Role of Active Chlorine Species

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Supporting Information

Table S1. Kinetic Balances and Steady State Concentrations of the Reaction Species.

Charge Balance	$I_{\text{cell}} = I_{\text{an}} = I_{\text{ca}}$ $I_{an} = I_{an}^{OH} + I_{an}^{O_2}$ $I_{ca} = I_{ca}^{H^+} + I_{ca}^{O_2 1} + I_{ca}^{O_2 4} + I_{ca}^{Cl^\bullet} + I_{ca}^{Cl_2^{\bullet-}} + I_{ca}^{ClO^-} = I_{ca}^{H^+} + I_{ca}^{O_2 1} + I_{ca}^{O_2 4} + I_{ca}^{Cl_2^{\bullet-}} + I_{ca}^{ClO^-}$
Reactive Species Balance	$[\text{rs}] = [\text{OH}^\bullet] + [\text{Cl}^\bullet] + [\text{Cl}_2^{\bullet-}] + [\text{ClO}^-]$
Kinetic Balance	$k_{\text{S}} = k_{\text{OH+S}} + k_{\text{Cl}^\bullet\text{+S}} + k_{\text{Cl}_2^{\bullet-}\text{+S}} + k_{\text{ClO}^-\text{+S}}$
Equilibrium	$>\text{Ti-OH}_2 \rightleftharpoons >\text{Ti-OH} + \text{H}^+ \quad (p\text{K}_\text{a} = 4.5)$ $>\text{Ti-OH} \rightleftharpoons >\text{Ti-O}^- + \text{H}^+ \quad (p\text{K}_\text{a} = 8.0)$ $\text{HOCl} \rightleftharpoons \text{ClO}^- + \text{H}^+ \quad (p\text{K}_\text{a} = 7.4)$ $\text{PhOH} \rightleftharpoons \text{PhO}^- + \text{H}^+ \quad (p\text{K}_\text{a} = 9.8)$
Steady-state Approximations	$[\text{OH}^\bullet]_{\text{SS}} = \dfrac{4\text{I}_{\text{an}} - \text{I}_{\text{an}}^{\text{O}_2}}{4\text{FV}(k_{\text{OH,Cl}}[\text{Cl}^-]_{\text{SS}})}$ $[Cl_2^{\bullet-}]_{SS} = \dfrac{k_{Cl,Cl}[Cl^\bullet]_{SS}[Cl^-]_{SS} - \dfrac{I_{ca}^{Cl_2}}{FV}}{k_{R_n,Cl_2}[R_n]_{SS}}$ $[ClO^-]_{SS} = \dfrac{k_{Cl}^{ClO}[Cl^\bullet]_{SS} - \dfrac{I_{ca}^{ClO}}{2FV}}{k_{OH,ClO}[\equiv Ti-{}^\bullet OH]_{SS} + k_{ClO}^{ClO_3} + k_{R_n,ClO}[R_n]_{SS}}$ $\dfrac{d[H_2]}{dt} = k_{H_2}[e^-]^2 = \dfrac{I_{ca}^{H_2}}{2FV}$ $\dfrac{d[O_2]}{dt} = k_{O_2}[\equiv Ti-{}^\bullet OH]^4 - k_{O_2/H_2O}^{r4}[O_2][H^+]^4[e^-]^4 - k_{O_2/H_2O}^{r1}[O_2][e^-]$ $= \dfrac{I_{an}^{O_2} - I_{ca}^{O_2 4} - 4I_{ca}^{O_2 1}}{4FV}$

$$\frac{d[CO_2]}{dt} = k_{CO_2}[R_{n+1}][Ox]$$

Table S2. Reaction Constants of $Cl^{\bullet}$ and $Cl_2^{\bullet-}$ for Substrates

Substrate	$k_{Cl^{\cdot}}$	$k_{Cl_2^{-\cdot}}$
H_2O	2.5×10^5 s^{-1}	1.3×10^3 s^{-1}
t-BuOH	6.5×10^8 M^{-1} s^{-1}	< 700 M^{-1} s^{-1}
$HCOO^-$	1.3×10^8 M^{-1} s^{-1}	1.9×10^6 M^{-1} s^{-1}
EtOH	7.5×10^8 – 1.5×10^9 M^{-1} s^{-1}	4.5×10^4 M^{-1} s^{-1}
Me_3COH	7.0×10^8 – 1.5×10^9 M^{-1} s^{-1}	7.0×10^2 M^{-1} s^{-1}
Acetic acid	2.0×10^8 – 6.0×10^8 M^{-1} s^{-1}	2.2×10^3 M^{-1} s^{-1}
Fumaric acid	3.0×10^9 M^{-1} s^{-1}	2.0×10^5 M^{-1} s^{-1}
Phenol	2.5×10^{10} M^{-1} s^{-1}	2.5×10^8 M^{-1} s^{-1}